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The Colloid Chemistry of Silica

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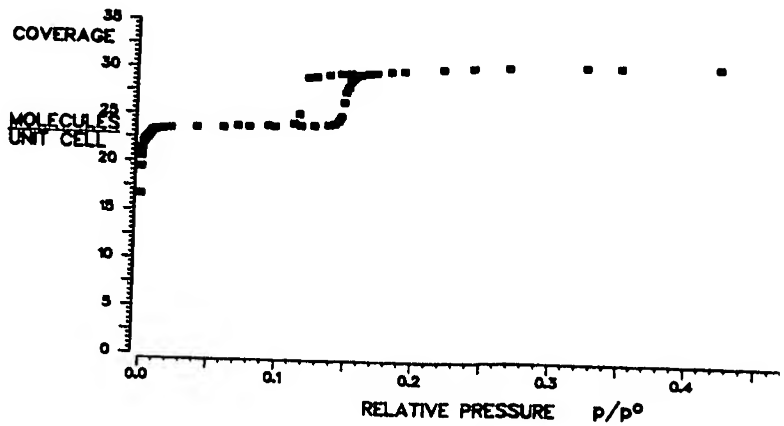

Figure 9. Adsorption isotherm of nitrogen at 77 K on silicalite-I obtained w conventional gravimetric sorption equipment. (Reproduced with permissi from reference 46. Copyright 1990.)

silica suspensions of varying pH. The isoelectric point was measured between pH 1 and 2 (*48*). Above pH 2 the particles are negatively cha below pH 1 the particles bear a positive charge. In one study isoelectric point of silica was reported to be at about pH 5 (*49*). Recent chromatographic-grade silica (Zorbax RX) became commercially avail and it exhibits distinct anion-exchange properties at about pH 5 (*50*). origin of this peculiar behavior is not yet clear.

Surface Functionality. Several groups contribute to Brøn acidity, as free (isolated), paired (geminal), and hydrogen-bonded (vici hydroxyl groups. Bridging hydroxyl groups in microporous amorpl silicas may also contribute (*51*). They are identified by their absorp bands in the frequency region between 3000 and 4000 cm^{-1} and by and ^{1}H CP-MAS NMR spectroscopy. Much attention has been pai geminal hydroxyl groups, which were first postulated by Peri (*5*).

Geminal hydroxyl groups have been shown to exist at the surfac Aerosil 200 even at high thermal pretreatment of 1073 K (*34*). Gem hydroxyl groups are formed as a result of acid treatment of amorph porous silicas (*42*). Geminal hydroxyl groups have been found to be m reactive in chemical surface modification of amorphous porous silicas t free hydroxyl groups (*8*).

The relative proportion of the hydroxyl groups heavily depends on method used for estimation. The relative content varies from silica to sil depending on the manufacturing process and after-treatment conditio

The total concentration of surface hydroxyl groups at a fully hydrox ated surface has been assessed to be about 5 per square nanomet

independent of the type of silica (*52*). The concentration decreases monotonically with increasing temperature when silicas are thermally pretreated under vacuum. Physisorbed water is first removed at temperatures between 380 and 420 K. Simultaneously, hydrogen-bonded hydroxyl groups condense to strained siloxane groups, which act as Lewis sites according to equation 1.

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 OH       OH     -H2O             -                      O
 |        |                  +    O                    /   \
 Si   +   Si     ----->      Si   Si    ----->       Si     Si
/|\      /|\                /|\  /|\                /|\    /|\
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Strained siloxane groups are formed up to about 770 K and then convert into stable siloxane groups (*53*). Strained siloxane groups completely rehydroxylate upon exposure to water, whereas stable siloxane groups rehydroxylate slowly. With the removal of hydroxyl groups and the formation of siloxane groups, the silica surface loses its hydrophilic character and becomes hydrophobic. The movement of the hydrophilic to hydrophobic character can be followed by measuring the heats of adsorption of water and other polar adsorptives.

The protonic sites at the surface of amorphous silica are weakly acidic compared to the acid centers in crystalline aluminosilicates (e.g., zeolites). On ZSM-5, Brønsted sites are formed by protons adjacent to aluminum atoms in the tetrahedral framework. The concentration of acid sites increases with the aluminum content. The total acidity as well as the acid strength distribution can be determined by using *n*-butylamine and Hammet or arylmethanol indicators (*25*). Depending on the pK_a of the indicator, a relative scale of the strength distribution is obtained (*54*). Results for a series of amorphous porous silicas of graduated pore size are shown in Figure 10. The acidity varies between pK_a −1 and +9 and is nearly the same for all silicas studied. The results are specifically valid for this method only and cannot be compared with those derived from other methods.

One of the major factors that determines the acidity values is the accessibility of surface sites, which is a function of the pore size of the silica, the surface morphology, and the size of the amine molecule used for the acidity assessment (*54*). A great deal of work has been carried out to elucidate the chemical and geometrical heterogeneity of the silica surface. The geometrical heterogeneity can be described by the fractal dimension *D*, which varies between 2 and 3 (*55*). The surface heterogeneity in terms of thermodynamic aspects can be visualized by the surface energy and the energy distribution (*56*). Appropriate functions are derived from potential energy equations that aid adsorption measurements. Although an enormous literature exists on the aspects of surface heterogeneity, this

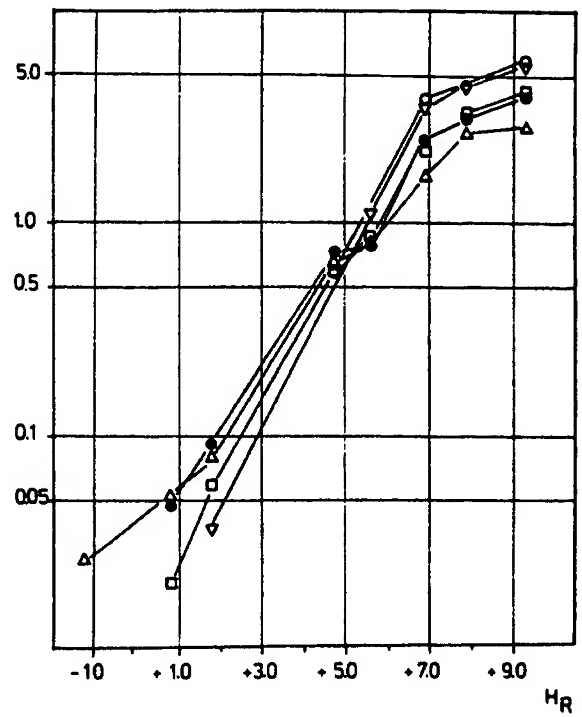

Figure 10. Cumulative acidity in micromoles per square meter on silica-20 (△), silica-40 (□), silica-60 (●), silica-100 (▽), and silica-200 (○) as a function of the acidity strength H_R*. (Reproduced with permission from reference 54. Copyright 1980.)*

approach has so far gained little importance in the evaluation of silicas in practice.

Conclusions

The silica surface represents a dynamic system that undergoes slight to notable changes depending on the conditions of the environment. To assess the dynamic character of the surface, studies are required that enable monitoring of structural changes during silica formation, after-treatment, use, and storage. Spectroscopic methods are the most suitable in this respect. In this context, the use of selected probe molecules embedded, adsorbed, or chemically bonded opens a new dimension in gaining substantial information and is exemplified by photophysical studies. A particular focus will be on in situ measurements to directly monitor subtle structural properties of the surface. The combined applica-